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Occurrence of trona in alkaline soils of the Indo-Gangetic Plains of Uttar Pradesh (U.P.), India

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Efflorescent crusts consisting predominantly of the sodium carbonate minerals trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) with minor thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) are commonly developed on less vegetated portions of the Indo-Gangetic Plains of the state of Uttar Pradesh in India. Being highly soluble, the presence of trona alone explains the high alkalinity of the soil (pH 10.5). Occasional flooding followed by fast evaporation in this extensive flood plain is a possible cause of the formation of this mineral. Carbonate build-up will have a major impact on the Gangetic ecosystem in the future, causing declining bioproductivity.

Introduction

Extensive occurrences of alkaline soils have been reported from the Indo-Gangetic Plains, a flood plain of the river Ganges, in northern India (Tamhane, 1954; Krishnan, 1956; Wadia, 1966; Shahid et al., 1994; Sharma et al., 2000). Samples of soils, from Kathanai (local meaning: difficult land) near Allahabad in the state of U.P. were collected from different depths (surface to 4 cm, 4–10 cm, 10–20 cm, 20–30 cm and 30–40 cm). The agricultural history of the region suggests that these high alkaline and sodic lands have been left unproductive in this area for a long time. Earlier studies related to this terrain have been confined to attempts to regenerate the alkaline and sodic soils for agricultural use. This study was conducted to identify a potential cause for such alkalinity of these soils. The equilibrium pH of soil solutions measured in 0.01 M CaCl_2 solution is 10.2–10.5. The area experiences intermittent dry and rainy seasons throughout the year. It was noticed during the field seasons that considerable rainfall (160–200 cm/yr) is followed by fast evaporation, which leaves behind a white encrustation (Figures 8 and 9) on the soil surface (to a maximum depth of about 10 cm). Due to high salinity and alkalinity of the soil there is minimal bioproductivity. Plant roots are commonly coated with a white substance almost everywhere in this region.

Identification of trona

This study identified trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) as a major phase in these soils. The mineral in the form of efflorescence, occurs mostly in the low-lying areas. It consists of a white crust that develops on the sandy surface and on any porous material (e.g. wood) embedded in the soil. The underlying sandy substrate is often damp.

The development of efflorescence is confined to areas where vegetation cover, mainly grass, is sparse, i.e. ground that receives full sunlight for most of the day. The crusts often exhibit contraction effects and in part detach from the underlying sandy substrate as small circular or elongated plates. The organic matter content of this soil ranges between 0.1–0.2 %.

Monoclinic single crystals and clusters of randomly arranged crystals of trona are both observed by secondary electron imaging using a JEOL JXA 8600 electron microprobe and a Hitachi S-4500

Figure 1 SEM photomicrographs of skeletal trona crystals, a single broken crystal showing hollow interior and thin walls.

Figure 2 (a) General views of ends of the skeletal crystals showing square cross-sections. (b) A rosette arrangement of a cluster of trona crystals (radiating arrangement).

Figure 3 Single trona crystal lying on a matrix of silica. Association of trona with quartz is quite common in these soils.

Figure 4 Skeletal crystals of trona showing solid walls, with filled interiors, found at a depth of about 10 cm.

Figure 5 X-ray diffraction powder pattern of the surface soil (0–4 cm), measured in Co-K alpha source. (Tr = trona; Q = quartz; Ab = albite; Th = thermonatrite; C = calcite; Nh? = nahcolite)

Figure 6 Sodium carbonate phases in equilibrium with a saturated solution as a function of CO_2 content of the gas phase and temperature. CO_2 content of present day air is plotted on right (after Eugster, 1971).

Figure 7 Phase diagram for the portion of the sodium carbonate, sodium bicarbonate, water system at 25 °C. Trona saturation occurs at B (after Eugster, 1971).

Figures 8 and 9 Field photographs of white encrustation of trona beside a dug pit. Depth of occurrence of trona is only upto 10 cm from surface. Arrow in Figure 8 indicates such encrustation.

field emission SEM operated at 5–10 kv. Individual crystal columns are 50 microns in length (Figure 1) and sometimes they form a rosette pattern (Figure 2) in their arrangement. This mineral occurs on the surface of the soil to a depth of about 10 cm, either forming clusters on the silica rich matrix (to a depth of 4 cm) (Figure 3) or as individual disseminated crystals to a depth of 10 cm in the soil profile (Figure 4). EDX analysis shows the presence of C, O, Si, Na and Al. The ratio of Na : O is a close approximation to the stoichiometric value for trona. Most Na retains in the carbonate phase in surface soils. The skeletal single crystal shown in Figure 1 and some of the disseminated crystals shown in Figure 2 exemplify hollow crystals that develop because their outer walls grow faster than the cores. Occurrence of such skeletal crystals is important because they represent growth that follows the reverse pattern of normal growth (Alena et al., 1990). Hollow crystals of trona were reported in the work of Jones et al. (1996). Similar crystals observed in these U.P. subsoils have a square to rectangular cross section. The presence of calcite was also noted in the bulk soil from SEM though the surface soils,

which contain more trona, are depleted in calcite. Five essential peaks for trona were identified by X-ray diffraction. They are 2.639Å, 3.062Å, 4.876Å, 9.7016Å and 2.4384Å (Figure 5). Other crystalline phases were identified as quartz, albite and calcite and two low-intensity peaks were identified for the mineral thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) as well. Based on this evidence it is provisionally concluded that this soil is mostly rich in trona (among the carbonate phases) and possibly thermonatrite as well. Semi quantitative estimate of trona in the soil (calculated from relative peak height in XRD spectrum) is 18.7 %. Peaks of calcite were not prominent in the surface soils (Figure 5). Gypsum, a common evaporite mineral in these settings (Whittig et al. 1982) was not identified from the U.P. soils. So the assemblage of trona and thermonatrite with minor calcite is important for this soil behavior.

Chemical conditions for forming trona

Green River Basin (Bradley, 1969), Lake Magadi (Eugster, 1971), Searles Lake (Eugster et al., 1965) are the three best-known trona deposits in the world. Dapeng et al. (1986) reported occurrence of trona from Nei Mongol Plateau of China distributed in desert and semi-desert areas. As reported by Eugster (1971) and Eugster et al. (1979), the mineral trona alone can be responsible for the pH of a solution above 9 because of the presence of necessary concentration of the carbonate ions. The high solubility of trona (Monnin et al., 1984; Given, 1985) contributes toward most of the alkaline properties of the soil. Two conditions must be satisfied to produce extensive trona formation: one is the existence of a closed basin and the other is sufficient perennial inflow to allow solutes necessary to form a salty lake/deposit (Eugster, 1971). The inflow for the U.P. soils is provided mainly by rainfall during the monsoons and the closed basin is achieved as rainfall collects in low areas. Infiltration is inhibited by the presence of an impermeable layer at a depth of about 1m.

The following scenario explains the thermodynamic stability of forming trona on the surface of the terrain. The dry soil surface, consisting of trona, is first flooded with the runoff waters at the onset of every rainy season. Dissolved trona provides most of the solute load of this surface brine. At the end of the rainy season, fast evaporation leads to drying, with trona precipitating during the drying process. This is only possible if the surface brine has degassed its CO_2 to the atmosphere (Eugster, 1971). Crystallization of sodium carbonates and bicarbonates from natural waters is controlled by dissolved CO_2 and temperature (Figure 6). The kinetic effects, especially those governing equilibration between dissolved and atmospheric CO_2 , are extremely important in determining the final form of the carbonates (Eugster, 1971; Whittig et al., 1982). At higher temperatures, natron is replaced by thermonatrite (see Figure 6).

The phase relationships illustrating the effects of evaporative concentration of sodium carbonate brines at 25°C are illustrated in Figure 7. Evaporative concentrations under conditions of equilibrium with atmospheric CO_2 will follow path AB in Figure 7. At B, trona will begin to crystallize. Crystallization of trona together with further evaporation should result in the solution composition moving towards C, i.e., it will cause a decrease in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ ratio, because this ratio in trona is greater than that in the solution. However, if equilibrium with atmospheric CO_2 is maintained, this ratio is buffered, and only trona is produced, because addition of atmospheric CO_2 stabilizes the $\text{HCO}_3^-/\text{CO}_3^{2-}$ ratio as follows:

Under conditions where atmospheric disequilibrium is promoted, i.e., where the $\text{HCO}_3^-/\text{CO}_3^{2-}$ ratio is not buffered, path BC is followed, producing thermonatrite and trona at C. The removal of HCO_3^- along BC under these conditions causes a marked rise in the pH, as the solution compensates for HCO_3^- removal by the reaction,

In spite of this compensation, the $\text{HCO}_3^-/\text{CO}_3^{2-}$ ratio falls well

below that of atmospheric equilibrium (e.g. Figure 6). The kinetics of equilibration are such that, during rapid evaporation, equilibrium with atmospheric CO₂ is not normally maintained (Hardie et al., 1970).

Conclusion

In conclusion, trona alone or possibly a mixture of trona and thermonatrite, which crystallize as a surface efflorescence on flood plains of the river Ganges, represent the end product of evaporative concentration of seasonal flood waters mixed with the local groundwater drawn up within the soils by capillary action. In the process of evaporation, calcite precipitation occurs below the surface, whereas trona and thermonatrite form on the surface. Crystallization of salts raises the pH of near-surface soil to 10.5. Carbonate accumulation has a serious impact on the growth of vegetation. This raises an important question to be solved in future in regard to the vegetation density in this terrain to understand whether the surface efflorescence occur as a result of sparse vegetation or the paucity of the vegetation is due to the presence of high salt concentrations. But the overall bioproductivity of the land has been affected greatly by this condition. This study pointed out a reason for such high alkalinity of the soils of U. P., India.

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